Vibrational Energy Transfer of Some X_2CO-type Molecules on Collision with Argon

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Vibrational excitation of X_2CO-type polyatomic molecules (X=F, Cl, Br, and H) on collision with an argon atom at temperatures 1000—3000 K was treated by the SSH-Tanczos method with a more tractable formula of average vibrational factor. Bending modes are more easily excited than bond-stretching modes in carbonyl halides. Excitation of the carbonyl stretching mode, the most difficult to occur in T–V process, becomes realizable when coupled with other modes to satisfy the near-resonance conditions.

Energy transfer involved in molecular collision is of importance in chemical reactions. Theories have been developed considerably for diatomic molecules[1–6)] but not much for polyatomic molecules. An approximation method was given by Schwartz, Slawsky, and Herzfeld (SSH[4,5)]), and Tanczos.[6)] Though it is based on the two-state distorted-wave approximation by the harmonic oscillator model, useful results can be deduced for the energy transfer process of vibrationally excited molecules.

We have applied this method to the vibrational excitation of X_2CO-type polyatomic molecules (X=F, Cl, Br, and H) on collision with an argon atom. From the results, the kinetic data of the thermal decomposition of carbonyl fluoride reported by Modica[7)] are discussed.

Method of Calculation

According to the SSH theory,[4,5)] the probability that a pair of molecules originally in vibrational states i_a and i_b will arrive at vibrational states f_a and f_b after a collision at temperature T K is given by

$$\begin{aligned}\langle P(\mathrm{a,b})\rangle &= \tilde{p}\,p_0(\mathrm{a})p_0(\mathrm{b})V^2(\mathrm{a})V^2(\mathrm{b})\\ &\times 8\sqrt{\frac{\mu}{2\boldsymbol{k}T}}\exp(\varepsilon_0/\boldsymbol{k}T)\left(\frac{8\pi^3\mu\Delta E}{\boldsymbol{h}^2}\right)^2\\ &\times\int_0^\infty F(u)\mathrm{d}u \end{aligned}\tag{1}$$

with

$$F(u) = \frac{u}{\alpha^4}(r_c/r_0)^2\exp\left(-\frac{\mu u^2}{2\boldsymbol{k}T}\right)\frac{\exp(H-H')}{[1-\exp(H-H')]^2}\tag{2}$$

and

$$H = \frac{4\pi^2\mu u}{\alpha\boldsymbol{h}},\quad H' = \frac{4\pi^2\mu v}{\alpha\boldsymbol{h}}\tag{3}$$

where μ is the reduced mass of the collision pair which approach each other with an effective relative velocity u and recede with a velocity v; ΔE is the net total change in translational energy involved during the collision, *i. e.*,

$$\begin{aligned}\Delta E &= \boldsymbol{h}\nu_a(i_a-f_a) + \boldsymbol{h}\nu_b(i_b-f_b)\\ &= \mu(v^2-u^2)/2\,;\end{aligned}\tag{4}$$

ε_0 is the minimum value of the Lennard-Jones potential

$$\varepsilon(r) = 4\varepsilon_0[(r/r_0)^{12} - (r/r_0)^6]\,;\tag{5}$$

α is an intermolecular force constant in reciprocal length units, for the repulsive exponential potential function

$$V(r) = V_0\exp(-\alpha r) - \varepsilon_0\tag{6}$$

evaluated so as to best fit Eq. (5) at $r=r_0$ and $r=r_c$, where r_c is the distance between molecular centers at the classical turning point for each u; p_0 is the geometrical factor required for the orientation consideration, $p_0(i_a\rightarrow f_a)=2/3$ being assumed herewith, and $\tilde{p}$ is a cross-section factor which is approximated by

$$\tilde{p} = 1.364/(1+1.1\,\varepsilon_0/\boldsymbol{k}T)\tag{7}$$

The average vibrational factor V^2 in Eq. (1) for polyatomic molecules has been given by Tanczos[6)] as follows:

$$V^2(\mathrm{a}) = V^2(i_a\rightarrow i_a\pm1) = \frac{\boldsymbol{h}\left(i_a+\frac{1}{2}\pm\frac{1}{2}\right)}{8\pi^2\nu_a}\frac{(\alpha^*)^2}{N_s}\sum_s\frac{A_{sa}{}^2}{m_s}\tag{8}$$

where s denotes the atom to be taken into account in the breathing sphere model, N_s the number of atoms, $N_s=4$ being assumed herewith, m_s an atomic mass, and A_{sa} the Cartesian displacement coefficient of s in the normal vibration Γ_a whose vibrational frequency is ν_a. α^* is evaluated at $u=u^*$, the most favorable velocity for the vibrational transition involving a particular value of ΔE:

$$\alpha^* = \frac{1}{r_0-r_c}\ln\left(1+\frac{E_m}{\varepsilon_0}\right)\tag{9}$$

where

$$E_m = \mu(u^*)^2/2 = \boldsymbol{k}T\left[\frac{2\pi^4\mu(\Delta E)^2}{(\alpha^*)^2\boldsymbol{h}^2\boldsymbol{k}T}\right]^{1/3}\tag{10}$$

Following the method of a normal coordinate analysis by Stretton,[8)] we can express the summation in Eq. (8) in a compact form as follows:

$$\sum_s A_{sa}{}^2/m_s = (\tilde{L}_X L_X)_{a,a}\tag{11}$$

where L_X is a transformation matrix between the orthogonal coordinate X and normal coordinate Q, and the product $(\tilde{L}_X L_X)_{a,a}$ is to be taken over the matrix elements corresponding to Γ_a only. L_X can be determined by means of the GF matrix treatment of molecular vibrations.[9)]

$$L_X = M^{-1}\tilde{B}L_G\Lambda_G{}^{-1/2}L_c\tag{12}$$

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where definitions of the matrices, M^{-1}, $\tilde{B}$, L_G, $\Lambda_G^{-1/2}$, and L_c are the same as in Ref. 9.

For the sake of convenience, we introduce the average amplitude factor $Y(X_s;\Gamma_a)$ for atom s in Γ_a:

$$Y(X_s;\ \Gamma_a) = (\tilde{L}_X)_{a,x_s}(L_X)_{x_s,a} + (\tilde{L}_X)_{a,y_s}(L_X)_{y_s,a} + (\tilde{L}_X)_{a,z_s}(L_X)_{z_s,a} \qquad (13)$$

The right-hand side of Eq. (11) can thus be written as

$$(\tilde{L}_X L_X)_{a,a} = \sum_s Y(X_s;\ \Gamma_a) \qquad (14)$$

We analyzed the in-plane vibrational motion of carbonyl halides and formaldehyde by using the potential function of Miyazawa.[10] We have omitted the mode Γ_6 (B_2 symmetry) throughout the calculation. Since it is the only mode corresponding to the out-of-plane motion, it cannot be mixed with the other five modes. Its omission does not affect our calculations. Molecular geometries were obtained from the literature.[11] Relevant Urey-Bradley force constants are summarized in Table 1.[12,13]

Vibrational transition probabilities of those molecules by translational-vibrational (T–V) or vibrational-vibrational (V–V) process on collision with an argon atom at T=1000—3000 K have been calculated by the above method. Relevant constants of the Lennard-Jones potentials for the collision pairs are given in Table 2. Calculations were carried out on a FACOM Computer at the Kyoto University Computation Center.

TABLE 1. UREY-BRADLEY FORCE CONSTANTS OF X_2CO MOLECULES IN md/Å[a]

Molecule	Force constants					
	K_{CX}	K_{CO}	H_{XX}	H_{OX}	F_{OX}	F_{XX}
F_2CO	4.528	12.85	0.450	0.294	1.578	1.120
Cl_2CO	1.99	12.61	0.11	0.218	0.860	0.523
Br_2CO	1.565	12.83	0.060	0.189	0.631	0.528
H_2CO	3.842	11.044	0.349	0.338	0.88	0.0

a) The symbols K, H, and F denote the force constants for the bond-stretchings, bond-bendings, and nonbond interactions, respectively. The coefficients for the energy terms linear with respect to displacements were all assumed to be one-tenth the force constants.

TABLE 2. LENNARD-JONES POTENTIAL PARAMETERS[a] AND REDUCED MASSES OF THE COLLISION PAIRS

Collision pair	r_0 (Å)	ε_0/k (K)	μ (10^{-23} g)
F_2CO-Ar	5.331	117.8	4.166
Cl_2CO-Ar	5.562	210.4	4.763
Br_2CO-Ar	5.638	253.9	5.448
H_2CO-Ar	4.988	116.8	2.869
CO-Ar	3.504	116.8	2.756

a) Potential parameters of carbonyl halides-argon systems were approximated by

$$r_0 = [r_0(\mathrm{CO-CO}) + r_0(\mathrm{X_2-X_2}) + r_0(\mathrm{Ar-Ar})]/2$$

$$\varepsilon_0 = \sqrt{\varepsilon_0(\mathrm{X_2-X_2})\varepsilon_0(\mathrm{Ar-Ar})}\,.$$

Parameter values of r_0(M–M) and ε_0(M–M) were taken from J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," John Wiley & Sons, New York, N. Y. (1954), Appendix.

Results and Discussion

Fundamental frequencies and average amplitude factors of all the molecules are summarized in Table 3.

TABLE 3. FUNDAMENTAL FREQUENCIES[a] AND AVERAGE AMPLITUDE FACTORS[b]

Molecule		$Y(X_s;\Gamma_a)$				
		Γ_1	Γ_2	Γ_3	Γ_4	Γ_5
F_2CO	$\tilde{\nu}$	1925 (1928)	968 (965)	580 (584)	1228 (1249)	622 (626)
	C	0.322	0.052	0.033	0.373	0.032
	O	0.129	0.111	0.043	0.003	0.156
	F	0.001	0.094	0.129	0.038	0.082
Cl_2CO	$\tilde{\nu}$	1819 (1827)	561 (567)	282 (285)	843 (849)	435 (440)
	C	0.297	0.107	0.033	0.429	0.000
	O	0.150	0.128	0.035	0.019	0.213
	Cl	0.000	0.037	0.071	0.007	0.036
Br_2CO	$\tilde{\nu}$	1819 (1828)	427 (425)	180 (181)	754 (757)	348 (350)
	C	0.295	0.150	0.021	0.438	0.018
	O	0.152	0.168	0.022	0.034	0.262
	Br	0.000	0.009	0.034	0.001	0.010
H_2CO	$\tilde{\nu}$	1742 (1744)	2805 (2780)	1483 (1503)	2865 (2874)	1242 (1280)
	C	0.262	0.027	0.009	0.044	0.108
	O	0.122	0.000	0.053	0.000	0.028
	H	0.437	2.802	2.488	2.700	2.097

a) Calculated and observed wavenumbers $\tilde{\nu}$ in $\mathrm{cm^{-1}}$. The experimental values for carbonyl halides (taken from Ref. 12) and formaldehyde (I. C. Hisatsune and D. F. Eggers, Jr., *J. Chem. Phys.*, **23**, 487 (1955)) are given in parentheses. b) $Y(X_s;\Gamma_a)$ given in units of $10^{23}\ \mathrm{g^{-1}}$.

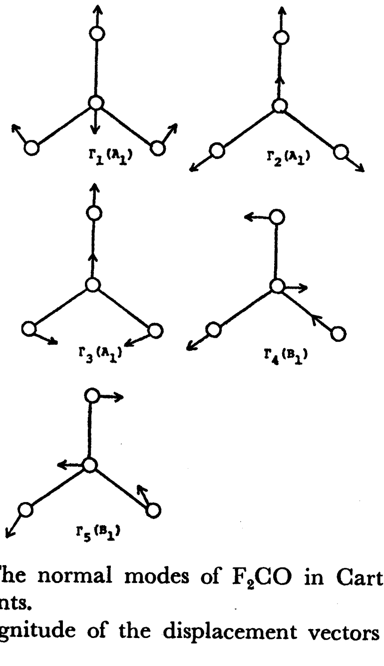

Fig. 1. The normal modes of F_2CO in Cartesian displacements.
The magnitude of the displacement vectors are arbitrary.

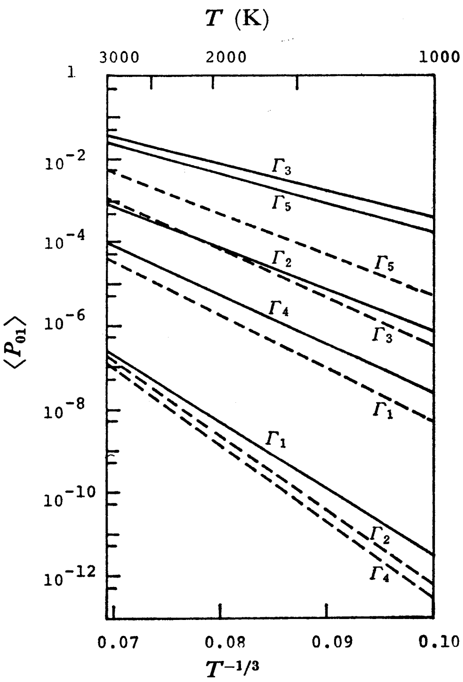

Fig. 2. Temperature dependences of the T-V vibrational transition probabilities, $\langle P_{01}\rangle$, of all the normal modes of F_2CO (solid line) and H_2CO (broken line).

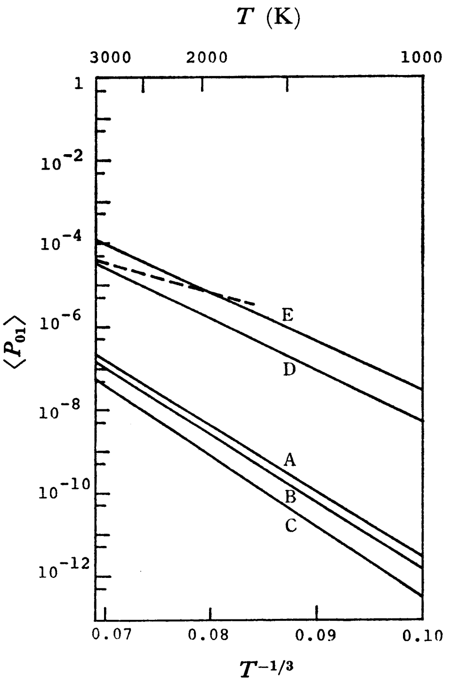

Fig. 3. Temperature dependences of the T-V vibrational transition probabilities, $\langle P_{01}\rangle$, of the carbonyl stretching mode (Γ_1) of X_2CO. The broken line represents the values calculated for CO from Eq. (15) with the aid of

$$\langle P_{01}\rangle = \exp(h\nu/kT)/\{\tau Z_c[1-\exp(-h\nu/kT)]\}$$

where Z_c denotes the average number of collisions which a CO molecule experiences per second under 1 atmospheric pressure.

A, F_2CO; B, Cl_2CO; C, Br_2CO; D, H_2CO; E, CO.

The normal modes of carbonyl fluoride in Cartesian displacements are represented in Fig. 1. There are three A_1 modes: carbonyl stretching Γ_1, symmetric CX stretching Γ_2, XCX bending Γ_3, and two B_1 modes: asymmetric CX stretching Γ_4, CO rocking Γ_5. It can be seen that vibrational wave numbers increase in the order $\tilde{\nu}_3<\tilde{\nu}_5<\tilde{\nu}_2<\tilde{\nu}_4<\tilde{\nu}_1$ for carbonyl halides and in $\tilde{\nu}_5<\tilde{\nu}_3<\tilde{\nu}_1<\tilde{\nu}_2\leqq\tilde{\nu}_4$ for formaldehyde.

Transition probabilities $\langle P_{01}\rangle$ for the 0—1 excitation of the various normal modes of carbonyl fluoride and formaldehyde by T-V process are plotted as functions of $T^{-1/3}$ in Fig. 2. As was the case with the vibrational excitation of diatomic molecules studied by Landau-Teller,[14] all the $\langle P_{01}\rangle$ are proportional to $\exp(-T^{-1/3})$. Transition probabilities of X_2CO molecules increase in the reverse order to that of the magnitude of vibrational wave numbers, *viz.*, $\langle P_{01}(\Gamma_1)\rangle<\langle P_{01}(\Gamma_4)\rangle<\langle P_{01}(\Gamma_2)\rangle<\langle P_{01}(\Gamma_5)\rangle<\langle P_{01}(\Gamma_3)\rangle$ for carbonyl halides, and $\langle P_{01}(\Gamma_4)\rangle\leqq\langle P_{01}(\Gamma_2)\rangle<\langle P_{01}(\Gamma_1)\rangle<\langle P_{01}(\Gamma_3)\rangle<\langle P_{01}(\Gamma_5)\rangle$ for formaldehyde. The results are due primarily to the decrease of ΔE in these orders.

Transition probabilities for the 0—1 excitation of carbonyl stretching modes (Γ_1) of carbonyl halides, formaldehyde, and carbon monoxide are shown in Fig. 3. As the vibrational wave number of carbon monoxide, we have assumed 2143 cm^{-1}.[13] Millikan *et al.* have observed that, in carbon monoxide–argon system, the vibrational relaxation time τ over 1700—3000 K is expressed by

$$\ln(p\tau) = \gamma T^{-1/3} + \delta \tag{15}$$

with $\gamma=182$ and $\delta=-22.4$, where p is in atm, τ in second, and T in K.[15,16] $\langle P_{01}\rangle$ of carbon monoxide obtained from this equation is also given in Fig. 3. The two values agree with each other especially near 2000 K. The $\langle P_{01}\rangle$ value for carbon monoxide is larger than the values for carbonyl halides by a few order of magnitude, despite its larger value of ΔE.

The average vibrational factors $V^2(0\to1)$ of the Γ_1 mode are given in Table 4. The V^2 values for carbon monoxide and formaldehyde are several times greater than those for carbonyl halides. This is ascribable to the larger values of α^* and smaller reduced masses of this mode for these two molecules. The reduced mass of the carbonyl stretching mode is indicated by $[(\tilde{L}_X L_X)_{\Gamma_1,\Gamma_1}]^{-1}$ for carbonyl halides as well as formaldehyde and $[m_C m_O/(m_C+m_O)]$ for carbon monoxide, where m_C and m_O denote the mass of the carbon and oxygen atoms, respectively.

TABLE 4. AVERAGE VIBRATIONAL FACTORS $V^2(0\to1)$ OF THE CARBONYL STRETCHING MODE

Molecule	$V^2(0\to1)\times10^3$				
	$T=1000$	1500	2000	2500	3000 K
F_2CO	2.01	1.99	1.99	1.98	1.98
Cl_2CO	1.96	1.94	1.93	1.92	1.92
Br_2CO	1.92	1.90	1.88	1.88	1.87
H_2CO	7.08	7.02	6.99	6.97	6.96
CO	9.30	9.22	9.18	9.15	9.13

However, with V^2 alone we cannot account for the large $\langle P_{01}\rangle$ value for carbon monoxide. An even more important contribution to $\langle P_{01}\rangle$ is derived from the reduced mass μ involved in Eq. (2); the $F(u)$ becomes greater in magnitude as the reduced mass decreases. The relatively large $\langle P_{01}\rangle$ for formaldehyde can be interpreted in the same way. All the results emphasize the concurrent importance of small ΔE and μ as well as large V^2 in order that vibrational energy transfer proceeds more effectively. The intramolecular motion of halogen atom in carbonyl halides hardly affects the vibrational excitation of carbonyl stretching mode; the amplitude factors of the halogen atoms in Γ_1 are negligibly small as compared with those for the carbon and oxygen atoms (Table 3).

Transition probabilities were calculated for the 0—1 excitation of carbonyl stretching mode by V–V processes coupled with the 1—0 de-excitation of the other modes $\langle P_{01}^{10}\rangle$, with the 2—0 de-excitation of the Γ_2 mode $\langle P_{01}^{20}\rangle$, and with the 1—0 de-excitation of both the Γ_3 and Γ_5 modes $\langle P_{10}^{01,10}\rangle$. The results for carbonyl fluoride are plotted as functions of $T^{-1/3}$ in Fig. 4.

We see that the transition probabilities $\langle P_{01}^{10}\rangle$ increase in the reverse order to that of the magnitude of ΔE, *viz.*, $\langle P_{01}^{10}(\Gamma_1-\Gamma_3)\rangle<\langle P_{01}^{10}(\Gamma_1-\Gamma_5\rangle<\langle P_{01}^{10}(\Gamma_1-\Gamma_2)\rangle<\langle P_{01}^{10}(\Gamma_1-\Gamma_4)\rangle$. A similar trend is also found in the case of formaldehyde: $\langle P_{01}^{10}(\Gamma_1-\Gamma_4)\rangle\leqq\langle P_{01}^{10}(\Gamma_1-\Gamma_2)\rangle<\langle P_{01}^{10}(\Gamma_1-\Gamma_5)\rangle<\langle P_{01}^{10}(\Gamma_1-\Gamma_3)\rangle$. Likewise, $\langle P_{01}^{20}\rangle$ is far larger than the corresponding $\langle P_{01}\rangle$ and $\langle P_{01}^{10}\rangle$ in the temperature range of our study. However, $\langle P_{01}^{10,10}\rangle$ is not so large as $\langle P_{01}^{20}\rangle$.

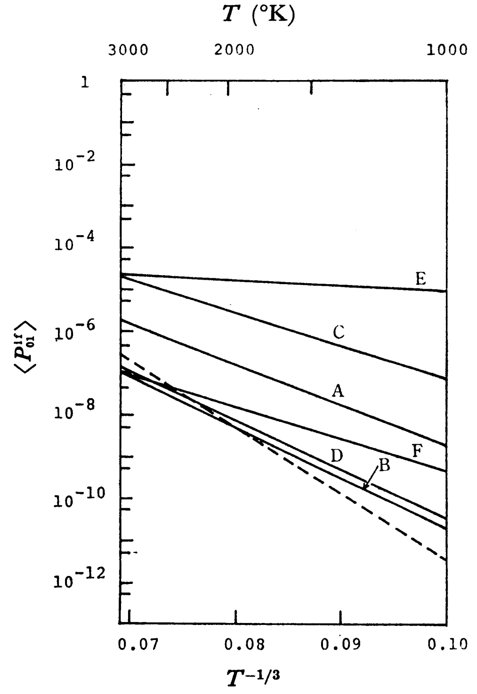

Fig. 4. Temperature dependences of the V-V vibrational transition probabilities, $\langle P_{01}^{10}\rangle$, $\langle P_{01}^{20}\rangle$, and $\langle P_{01}^{10,10}\rangle$ of F_2CO.
A, $\langle P_{01}^{10}(\Gamma_1-\Gamma_2)\rangle$; B, $\langle P_{01}^{10}(\Gamma_1-\Gamma_3)\rangle$; C, $\langle P_{01}^{10}\langle\Gamma_1-\Gamma_4)\rangle$; D, $\langle P_{01}^{10}(\Gamma_1-\Gamma_5)\rangle$; E, $\langle P_{01}^{20}(\Gamma_1-\Gamma_2)\rangle$; F, $\langle P_{01}^{10,10}(\Gamma_1-\Gamma_3, \Gamma_5)\rangle$.
The broken line indicates $\langle P_{01}\rangle$ for the T-V process.

In short, the transition probability for the 0—1 excitation of Γ_1 at lower temperature markedly increases on near-resonance coupling with another mode. Thus, it is probable that under the usual experimental conditions, vibrational excitation of a normal mode is caused mainly by a V–V process. At higher temperature ($T>2000$ K), however, none of the V–V processes are more efficient than the T–V process.

Modica[7] has studied the kinetics of shock-tube decomposition of carbonyl fluoride in argon at 2200—3600 K:

$$F_2CO + Ar \longrightarrow FCO + F + Ar.$$

He concluded that in the transition state the bending modes (Γ_3, Γ_5, and Γ_6) are considerably deformed in constrast to the relatively insensitive bond-stretching modes (Γ_1, Γ_2, and Γ_4). Our present calculations show the relative ease of the vibrational excitation of Γ_3 and Γ_5. The Γ_6 mode should also be as easily excited as these two modes because of its small vibrational wave number (774 cm^{-1}).[12] The decomposition reaction might proceed through the V–V energy transfer from these bending modes to the C–F bond-stretching modes.

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